

# Lithium-Sulfur Dioxide Batteries on Mars Rovers

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## ABSTRACT

NASA's 2003 Mars Exploration Rover (MER) missions, Spirit and Opportunity, have been performing exciting surface exploration studies for the past six months. These two robotic missions were aimed at examining the presence of water and, thus, any evidence of life, and at understanding the geological conditions on Mars. These rovers have been successfully assisted by primary lithium-sulfur dioxide batteries during the critical entry, descent, and landing (EDL) maneuvers. These batteries were located on the petals of the lander, which, unlike in the Mars Pathfinder mission, was designed only to carry the rover. The selection of the lithium-sulfur dioxide battery system for this application was based on its high specific energy and high rate discharge capability, combined with low heat evolution, as dictated by this application. Lithium-sulfur dioxide batteries exhibit voltage delay, which tends to increase at low discharge temperatures, especially after extended storage at warm temperatures. In the absence of a depassivation circuit, as provided on earlier missions, e.g., Galileo, we were required to depassivate the lander primary batteries in a unique manner. The batteries were brought onto a shunt-regulated bus set at pre-selected discharge voltages, thus affecting depassivation during constant discharge voltage. Several ground tests were performed, on cells, cell strings and battery assembly with five parallel strings, to identify optimum shunt voltages and durations of depassivation. We also examined the repassivation of lithium anodes, subsequent to depassivation. In this paper, we will describe these studies, in detail, as well as the depassivation of the lander flight batteries on both Spirit and Opportunity rovers

prior to the EDL sequence and their performance during landing on Mars.

## INTRODUCTION

NASA's on-going Spirit and Opportunity missions constitute twin robotic rovers, which were launched in June 2003 and landed successfully in the beginning of this year. Since then they have successfully completed the primary phase of the missions, and are about to complete the first extended phases, with about 175 and 150 Martian sols already completed, for Spirit and Opportunity, respectively. Several astounding scientific contributions have already been made by both these rovers, including detection of evidence of past water at the both the landing sites, located at opposite sides of the planet, Mars. Even though these two rovers are being well supported by low-temperature lithium ion batteries,<sup>1</sup> their successful landing could be attributed to the successful operation of the primary, lithium sulfur-dioxide batteries, located on the lander. These primary batteries ably and effectively assisted the Entry Descent and Landing (EDL) sequence, which includes critical operations, such as deployment of parachutes, firing of retro rockets, release of air bags, and finally, enabling the egress of the rover from the lander.

The selection of the lithium-sulfur dioxide system for this application was made based on a detailed trade-off study of available, high specific energy, aerospace primary batteries.<sup>1</sup> Even though the Li-SO<sub>2</sub> system has slightly lower specific energies compared to the lithium-thionyl chloride system, for example, it has a lower impedance, and thus lower heats of evolution at the high discharge rates, a critical

requirement resulting from the near-adiabatic discharge conditions prevalent on the lander. This paper briefly describes the lander batteries employed and their in-flight performance on both Spirit and Opportunity. Particular attention is focused on the voltage delay characteristics of these batteries and the strategies adopted to successfully depassivate these batteries, prior to the EDL sequence.

### Lander Li-SO<sub>2</sub> Batteries

The lander battery is comprised of five lithium-sulfur dioxide batteries, each with twelve D-size Li-SO<sub>2</sub> LSX cells stacked in three tubular cavities, machined from an aluminum block, and connected in series (Fig.1). The cells were made by SAFT America at Valdese, NC, and the battery was fabricated by SAFT America, Cockeysville, MD.

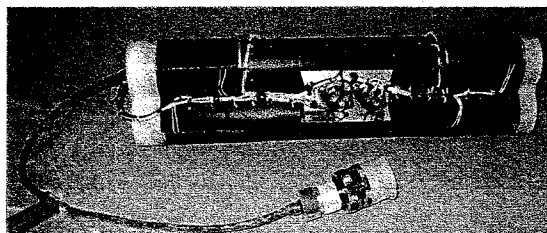


Fig. 1: One of the five parallel, Li-SO<sub>2</sub> batteries on MER, Spirit and Opportunity

Each of these batteries is equipped with heaters, thermostats, PRTs (platinum resistance thermometer), and current-limiting fuses. The batteries were maintained at -40°C during cruise, and warmed to 0°C before the EDL. The rationale for choosing a low discharge temperature was to limit the end discharge temperature, in the adiabatic conditions, to under 70°C. Furthermore, because of the superior performance at low temperatures, the LSX (low rate version) cells were preferred to LSH, the high-rate version. These five batteries were distributed on three lander petals and connected in parallel.

### Voltage Delay Of Li-SO<sub>2</sub> Batteries

The Li-SO<sub>2</sub> system, like many lithium primary battery systems, exhibits a phenomenon, known as voltage delay, which is a delayed

response of the battery to discharge.<sup>2</sup> During this period, the voltage drops instantaneously to low values, often below the allowable limit of 2.0 V/cell, and recovers over a short period of time, termed as voltage delay, to the expected values. This is a common feature of reactive metal anodes, such as Li, Mg and Al, and is attributed to the passive films present on the anode surfaces.<sup>3,4</sup> The films, being composed of electronically resistive materials, contribute to the ohmic polarization, which, in turn, contributes to the instantaneous voltage undershoot. The breakdown of the passive film, either by the local high electric field applied on discharge or by the mechanical stresses generated by the discharge products, exposes the metal underneath and thus aids in the recovery of cell voltage. The voltage delay increases with: 1) an increase in discharge current, 2) a decrease in temperature and 3) with storage. The voltage delay will also be evident, whenever the discharge current is increased, due to the need for depassivating a larger area of the anode to support the desired current density. Furthermore, the voltage delay characteristics will reappear during rest, after discharge, due to reformation of the passive film from the reaction of anode with electrolyte species.<sup>5</sup>

An engineering solution to the voltage delay of the lithium primary batteries is to adopt a depassivation circuit that would affect battery discharge, prior to actual use. This would be a brief discharge through a resistor maintained at warm temperatures, as implemented successfully on Galileo,<sup>6</sup> Mars Pathfinder Sojourner,<sup>7</sup> and is available on Stardust. This was, however, not provided on the Mars Exploration Rovers, with the assumption that the load on the battery would increase rather gradually, over a period of ten minutes, during transition of the bus from solar array to the lander primary batteries, before the EDL.

### The Problem

During the first health checks on the lander batteries, towards the end of cruise and a couple of months before EDL, it was realized, as also determined from ground testing of engineering models, that the lander batteries

showed voltage delay characteristics, serious enough to cast some doubts on their ability to handle the EDL loads adequately. The voltages dipped to  $\sim 22$  V, albeit at lower temperatures of  $\sim -20^\circ\text{C}$ , at a modest load of 120 Ohms, corresponding to 250 mA. There was a delay of about 2-3 seconds, before voltages attained values higher than 24 V, the usual battery cut-off voltage (Fig. 2).

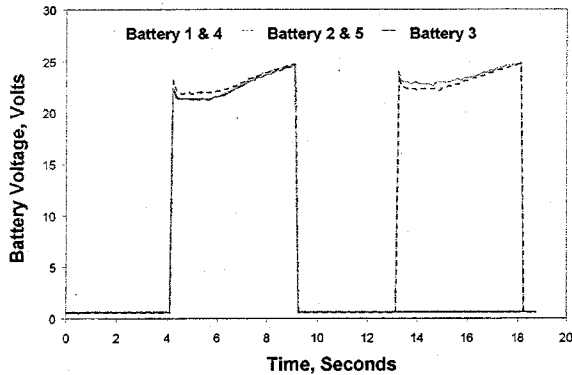


Fig. 2: Voltage delay, as part of health check, of the Spirit primary batteries, towards the end of cruise, at 120 Ohms and  $\sim -20^\circ\text{C}$ .

The observed voltage drop is expected and consistent with the voltage delay characteristics of Li-SO<sub>2</sub> cells at 250 mA (Fig. 3). Nevertheless, the implications of such behavior could be serious from the mission perspective.

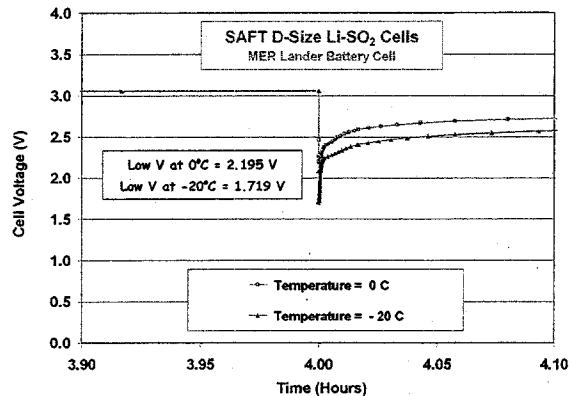


Fig. 3: Voltage delay of MER Li-SO<sub>2</sub> cells at 0.5 A at  $0^\circ\text{C}$  and  $-20^\circ\text{C}$ .

In the nominal mode, the lander batteries would be on bus just before the Turn to Entry (TTE), when the solar array would start turning further away from the Sun. Since the

lander batteries couldn't support the loads during the voltage delay, the loads on the solar array would increase, which in turn would bring down the solar array voltage. This could eventually result in a solar array collapse. Furthermore, during the voltage undershoot, two voltages are critical: a) 22 V, which triggers the POR (Power Off Reset), and b) 26 V, below which the Rover battery will be brought onto the bus for supporting the EDL. This would deplete the rover battery assembly unit, reducing its margins for surface operations after landing. The minimum lander battery voltage should therefore be above 26 V, corresponding to about 2.3 V/cell, which is a relatively high cut-off voltage for the Li-SO<sub>2</sub> cell. Appropriate strategies were thus to be identified to mitigate this voltage delay and be implemented on the MER missions.

#### Depassivation by multiple low-current discharge pulses.

Since there was an option to discharge the batteries across a 120  $\Omega$  load for 5 seconds, as part of the health check, we examined the possibility of achieving the desired depassivation, using such multiple 5-second pulses. Table-1 summarizes the voltage delay characteristics after depassivation from several such multiple pulses, with a rest period of fifteen seconds between successive pulses.

Cell Number	Number of pulses applied prior to 2A load	Low Voltage Recorded (2A Load)	Time until reaching 2.3 V (2A Load)
AO 1806	0	1.765 V	9.6 seconds
AO 0973	5	1.673 V	11.3 seconds
AO 1776	10	1.911 V	6.1 seconds
AO 1807	15	1.874 V	8.1 seconds

Table 1: Voltage delay characteristics of MER Li-SO<sub>2</sub> cells, after multiple, low-current pulses.

As may be seen from the table, the cells, even after the above pulsing protocol, exhibit fairly long voltage delay at 2 A, of over 8 seconds to a voltage of 2.3 V, with a minimum voltage of  $\sim 1.8$  V. Based on

these results, it was concluded that this mode of depassivation was not adequate for the MER mission.

### Depassivation via Potentiostatic or Constant-voltage Discharge

The only option available for us on the MER mission was to bring the lander batteries onto the shunt-regulated bus and bring down the shunt voltage to low values, corresponding to the discharge voltage of the lander batteries. It may be possible to achieve depassivation by constant-potential discharge. However, there aren't any reports in literature on such constant-voltage depassivation. Further, there are striking differences between constant-voltage depassivation or and constant-current/load depassivation, as discussed below.

In a constant-current discharge mode, and to a large extent in constant-load discharge, the electric field generated across the passive surface film is fairly large. For example, for a one-volt drop in the cell voltage across the passive film, which is typically 10-100 nm, will be 0.1-1 MV/cm. Such high electric fields would readily induce a breakdown of the dielectric films.<sup>8</sup> In a potentiostatic discharge, on the other hand, the electric field applied is considerably smaller; at 2.8 V, for example, the electric field will be a 10-100 kV/cm. The voltage delay is, therefore, less dramatic in constant current discharge, compared to constant-load discharge, which in turn is considerably less than in a potentiostatic discharge. Secondly, the shape of voltage is considerably different from the current delay observed in constant-voltage discharge, as illustrated below.

In examining the depassivation effects during potentiostatic discharge, we chose the initial temperature as anticipated on the spacecraft, i.e., 0°C. The depassivation procedure thus includes soaking the test cells at 0°C for at least 4 hours for thermal equilibrium, followed by constant potential discharge for a maximum duration of two hours, or until the cell current reaches a value of 3 A max. This

maximum current was dictated by the safety issues associated with Li-SO<sub>2</sub> cells at rates higher than C/2, especially under adiabatic discharge conditions, as well as by the currents the shunts and radiators could handle. The efficacy of depassivation was then verified using three constant current discharge pulses (0.50 A, 1.50 A, and 2.00 A) of 60 seconds with 15 seconds of rest in between. Furthermore, to assess permanence of the depassivation effect, due to a reformation of the surface films, these pulses were repeated at different time intervals. Fig. 4 illustrates the sequence of such events for a slow depassivation at 2.83 V.

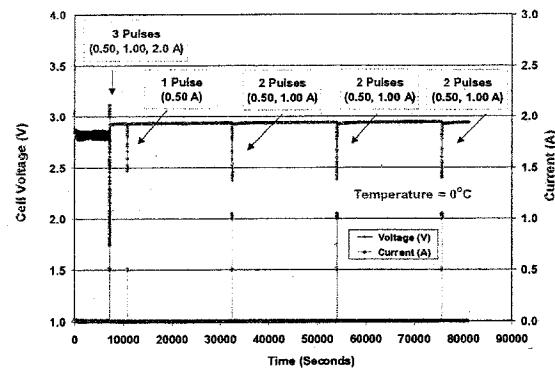


Fig.4: Sequence of events during depassivation of a Li-SO<sub>2</sub> cell at 2.833 V.

As may be seen from the above figure, the current never approached 3 A in the two hours of depassivation at this high voltage, suggesting incomplete depassivation. The voltages in the subsequent constant current pulses expectedly show low voltages of ~ 2.37 V. The results of depassivation at different voltages, i.e., at 2.833, 2.76, 2.70, 2.642, 2.575 and 2.53 V, which correspond to the available shunt voltages of 34, 33.12, 32.4, 31.7, 30.9 and 30.4 V, respectively, are summarized in Table-2.

De-Passivation Discharge Voltage (Potentiostatic)	Maximum Current on Potentiostatic Discharge (1.5 or 3.0 A Max.)	Potentiostatic Discharge Time	1st 0.5 A Pulse (Low V)	1st 1.5 A Pulse (Low V)	1st 2.0 A Pulse (Low V)
2.533	3.000 A	0.161 hr	2.7915	2.6516	2.5986
2.575	1.500 A	0.214 hr	2.7314	2.5579	2.4958
2.575	3.000 A	0.418 hr	2.8093	2.6860	2.6368
2.642	1.500 A	1.01 hr	2.7793	2.6390	2.5863
2.642	2.49 A	1.258 hr	2.8324	2.7349	2.6960
2.700	0.412 A	2.0 hr	2.6752	2.4833	2.4144
2.760	0.028 A	2.0 hr	2.1549	1.7995	2.2371
2.833	0.010 A	2.0 hr	2.0305	1.7395	2.2208

Table-2: Depassivation at different voltages.

As may be seen from the above table, the Li-SO<sub>2</sub> cells can, be adequately depassivated via constant potential discharge. High shunt voltages of 34 V (2.833 V/cell) and 33.12 V (2.760 V/cell) do not provide adequate depassivation. On the other hand, low shunt voltages of 30.9 V (2.575 V/cell) and 30.4 V (2.533 V/cell) depassivate quite rapidly, such that the currents are high and could saturate the shunt stages, as illustrated in Fig. 5.

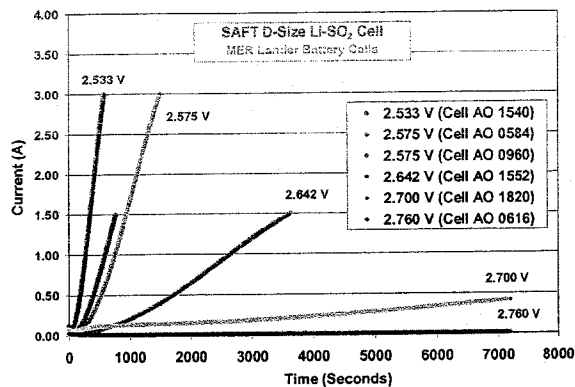


Fig. 5: Depassivation rates at different voltages.

Unlike the undershoots in the voltage during conventional constant-current or constant-load depassivation, the current during potentiostatic depassivation varies in a characteristic 'U' shape. The current drops initially and levels off, before exhibiting an eventual increase, to give a bathtub profile (Fig. 6).

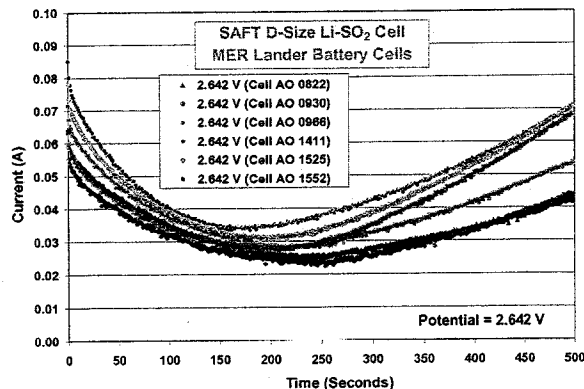


Fig. 6: Depassivation rates at 2.642 V, showing the bathtub profile in current.

It is interesting to note that, even during constant current depassivation, the voltage profile is similar to the behavior noted previously, when the currents are small enough, not to induce dielectric breakdown, as in galvanostatic non-destructive micropolarization.<sup>9-11</sup> The initial decrease in voltage or current may be attributed to the slow charging of the passive film capacitance.

It is clear from Fig. 5 and Table-2 that the optimum shunt voltages are 32.4 V (2.7 V/cell) and 31.7 V (2.642 V/cell), which were examined in further detail. Furthermore, based on several such measurements on various cells, the following inferences were made:

- Multiple depassivation cycles of 25 minutes each, instead of one continuous depassivation, are not only as effective, but are more advantageous from a ground control and thermal standpoint.
- Initial depassivation cycles at 2.642 V and subsequent milder depassivation cycles at 2.7 V are deemed complete, if the currents approach 3 A and 1 A, respectively.
- The depassivation is more rapid at 5°C, compared to 0°C. This is significant, since the flight batteries were under thermostatic control with a range of 0°C to 5°C.
- There is some degree of variation from cell to cell in depassivation characteristics, which is more noticeable at low shunt voltages.
- The depassivation can be implemented about twenty hours prior to EDL, such that the depassivation procedure would not interfere with the EDL protocol. Beyond 24 hours, however, the repassivation of Li may occur, contributing to a longer voltage delay.

#### Voltage Delay Tests on MER Batteries

The guidelines thus developed for testing at the string and battery levels, and for subsequent implementation on the MER spacecraft, include: 1) multiple depassivation cycles at 31.2 V (2.642 V/cell), of 25 minutes

each separated by one hour intervals, to allow for data communication to the ground and data evaluation time, till the current approaches 1.25 A, followed by 2) multiple depassivation cycles at 32 V (2.7 V/cell), of 25 minutes each with one hour interval, till the current approaches 1 A. However, if the end-current in the first step exceeds 3 A, the depassivation was treated as complete. These voltages were corrected for the voltage drops in both the cabling and at the diodes. A maximum of four such depassivation cycles would be implemented at these two voltages. About 20 hours after such depassivation, the battery was subjected to discharges at 1.0 A, 1.5 A and 2.0 A for five minutes each. Finally, a capacity check was performed on the battery, by continuing the discharge at 2 A to a cut-off voltage of 24 V.

Fig. 7 shows the depassivation behavior of a MER battery at 0°C. As may be seen from the figure, the current quickly approached 3 A after ~ 14 minutes (cumulative capacity: 0.52 Ah) into the first step, thus, skipping the second step of depassivation. The temperature rose to ~ 6°C during this depassivation.

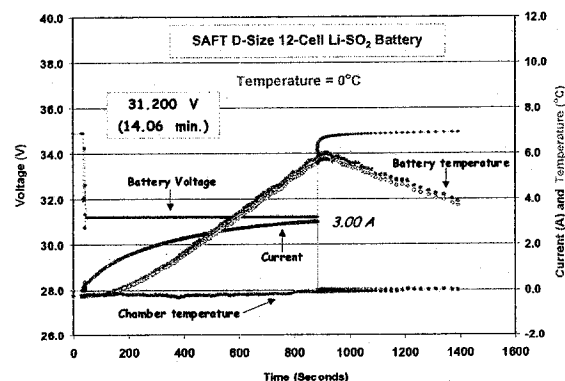


Fig. 7: Depassivation of a MER battery at 31.4 V and 0°C.

After 20 hours of rest, this battery exhibited lowest voltages of 28.811 V (or 2.403V/cell), 31.396 V and 31.310 V at 1.0, 1.5 and 2.0 A, respectively. The second battery tested under similar conditions, went through two cycles of depassivation at: 1) 31.4 V for 25 minutes, with a cumulative discharge capacity of 0.237 Ah corresponding to an ending current of 1.334 Amps, and 2) 32.0 V for 25 minutes with a cumulative capacity of 0.299 Ah and ending

current of 1.040 A. The lowest voltages on subsequent discharges, after 20 hours, were 28.64 V (or 2.387 V/cell), 31.21 V and 31.16 V, at 1.0 A, 1.5 A and 2.0 A, respectively. Both the batteries delivered total capacities close to 7 Ah, from the above test, including discharge at 2 A to 24 V, showing good energy margin for MER.

Finally, a similar test was performed on a battery assembly with five parallel batteries, with two strings at 5°C and three at 0°C, as would be the worst case on the spacecraft. The battery assembly was depassivated at 31.200 V for multiple (maximum of three) cycles of 25 minutes, or until the current approached 2.5 A. If the current exceeded 8 A, there would be no further depassivation; otherwise, the depassivation would be repeated at 32 V for multiple (maximum of four) cycles of 25 minutes, until the current approached 5A. Fig. 8 shows the depassivation of the battery assembly.

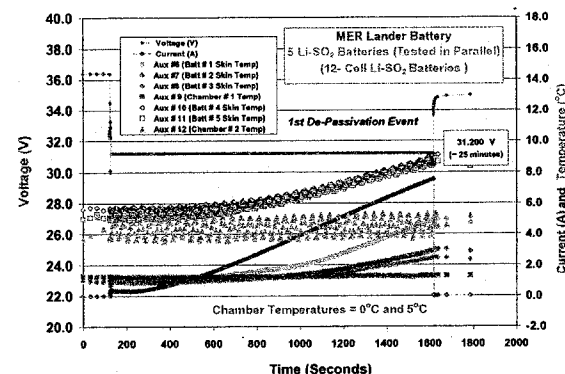


Fig. 8: Depassivation of MER Lander battery assembly at 31.4 V.

The lander battery assembly showed an ending current of 7.54 A after 25 minutes at 31.4 V, with a cumulative capacity of 1.38 Ah. The individual string currents, measured using shunts, ranged from 0.8 to 2.1 A. In the second depassivation at 32 V, the ending current was 5.76 A and the capacity 1.72 Ah. The string dispersion observed in current was reduced in this depassivation cycle. After 20 hours of open circuit storage, the battery was subjected to discharge pulses and the lowest battery voltages were 30.965 V, 30.730 V, 31.195 V and 30.141 V, at 2.5 A, 5 A, 7.5 A and 9 A, respectively. The constant current discharge, carried out at 9 A, after the above pulse measurements, showed

a cumulative capacity of 35 Ah for the battery under these conditions, showing an excellent energy margin for the mission (Fig. 9). The temperature rose by a maximum of 12 to 15°C during the course of this discharge.

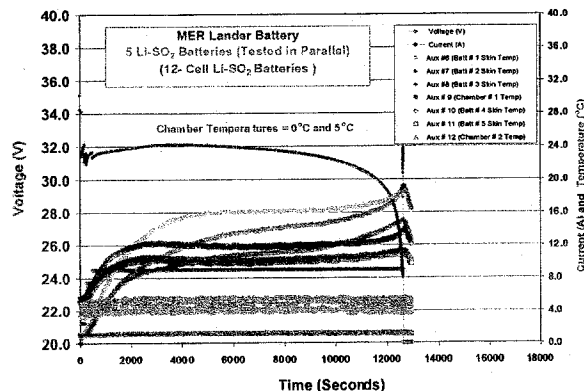


Fig. 9 Constant current discharge of MER lander battery assembly at 9 A, after depassivation and pulse testing.

### Flight Data from Spirit and Opportunity

Similar to the ground testing, the lander battery assemblies on both the Spirit and Opportunity Mars Exploration Rovers were conditioned prior to EDL. They were depassivated using a shunt voltage of 31.2 V for three cycles, each of 25 minutes duration. Fig. 10 illustrates the depassivation of lander batteries on the Spirit rover.

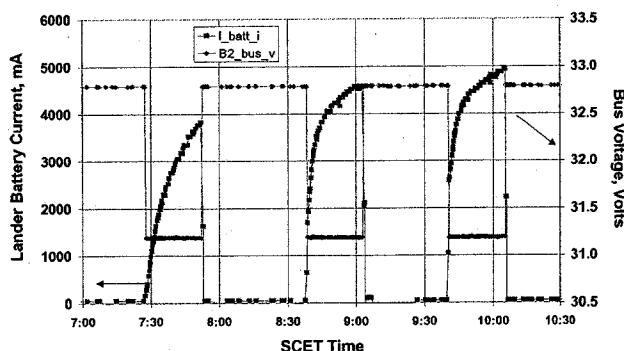


Fig. 10: Depassivation of MER Spirit lander battery assembly

As may be seen from the figure, the observed battery currents are lower than what would be expected from the laboratory tests on cells, strings and five-battery tests at a

depassivation voltage of 31.2 V. Also, the current is leveling off around 5 A even after multiple (three) depassivation cycles. It is possible that the line impedance is higher than estimated, thus making the depassivation milder. The battery health test showed healthy voltages of over 33 V (at 0.25 A). Based on the above, it was concluded that the Spirit lander batteries were sufficiently depassivated, as was confirmed from the EDL data (Fig. 11).

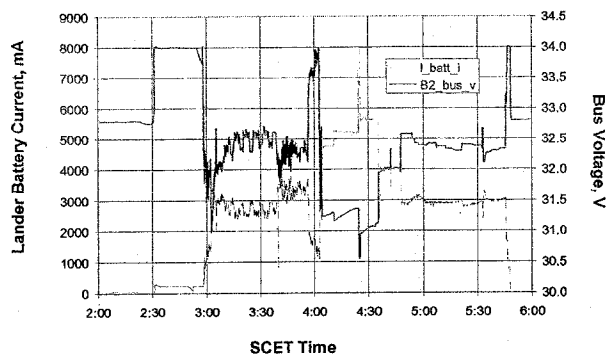


Fig. 11: Performance of the lander Li-SO<sub>2</sub> battery on MER Spirit during EDL.

As may be seen from the above figure, the battery voltages during EDL were around 32.5 V at an average load of 3 A. There were undershoots during changeover to higher currents, to about 8 A, but the lowest voltages observed were around 30.5 V, an excellent margin over the minimum required voltage of 26 V. Similar behavior was also observed in the case of lander batteries on the Opportunity rover (Fig. 12).

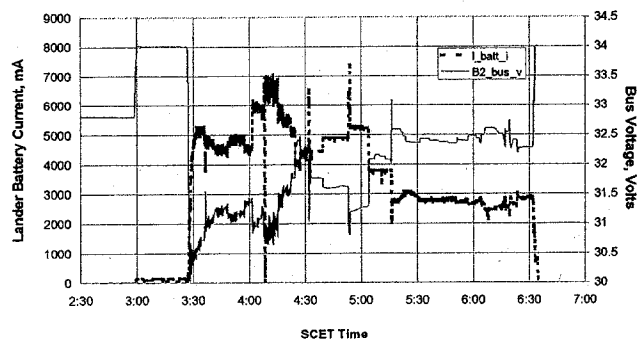


Fig. 12: Performance of the lander Li-SO<sub>2</sub> battery on MER Spirit during EDL

The average voltage, as well as the minimum voltage were lower on the

Opportunity rover, mainly due to a higher current of 5 A, compared to 3 A, in the case of Spirit.

In summary, it is appropriate to conclude that the successful landing of the rovers may be partly attributed to a successful depassivation of the lander batteries, prior to EDL, and their excellent performance during EDL.

### Conclusions

The Li-SO<sub>2</sub> primary batteries, located on the lander were designed to support the critical entry descent and landing operations of the Mars Exploration Rovers. There were concerns on the readiness of these batteries to meet the mission needs, due to their voltage delay. In order to depassivate these batteries and thus make them available for EDL, we adopted a new method of depassivation, via constant-potential discharge. Several experiments were carried out on the ground, on cells and later on batteries, to identify optimum shunt voltages and durations that would provide rapid and sufficient depassivation, without overloading the radiators. Such depassivation was affected several hours prior to EDL, thus not interfering with the EDL operations, while taking into account the repassivation effects. The procedures thus developed were successfully implemented on both the Spirit and Opportunity rovers, wherein the lander batteries ably supported the EDL and preserved the energy from the rover Li-ion rechargeable batteries for post-landing operations.

### Acknowledgements

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